

APPLICATION FOR UNITED STATES LETTERS PATENT

For

**THREE-DIMENSIONAL NANOTUBE STRUCTURE**

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## **THREE-DIMENSIONAL NANOTUBE STRUCTURE**

### **FIELD**

[0001] Embodiments of the invention relate, generally, to the field of nanotechnology and, more specifically, to nanotubes.

### **BACKGROUND**

[0002] Nanotubes (e.g., carbon nanotubes (CNTs)) are tubular molecules that exhibit high thermal and electrical conductivity. CNTs have a cylindrical structure with a diameter ranging from approximately 1 - 100 nanometers and a length of several microns or more. Each end of the cylindrical structure is capped with a half fullerene molecule.

[0003] The theoretical applications for CNTs include miniature cathode ray tubes (CRTs), to provide a thin, low energy, lightweight display, high strength composite materials, electronic circuitry, as well as superconductor and biotechnology applications.

[0004] Currently, applications for CNTs are developing that take advantage of their light-weight, high-strength, and electrical and thermal properties. Many such applications involve mixing the CNTs with other materials, for example, polymers. However, because CNTs are not readily soluble in many types of polymers and solvents, they tend to clump together making it difficult to obtain a uniform material with the desired uniform property.

[0005] For some applications, a random orientation of the CNTs is not desirable. For example, the excellent thermal conductive properties of the CNTs are extremely directionally dependent. That is, the tubular structure acts as a conduit for the heat so the heat moves readily along the orientation of the tube. Or for example, the CNTs may be used to form electrical interconnects. For such applications, a specific orientation may be

desired. Some progress has been made toward linking the individual CNTs together to facilitate orientation. Linking the individual CNTs allows for a greater ability to orient them in a desired direction.

[0006] Currently, the CNTs can be linked, one-dimensionally, by using an acid to sever each end of the tube. That is, the half fullerene molecule at the end of each tube is removed, resulting in an open-ended tubular structure. Each end of the open-ended tubular structure will have molecular bonding sites. Connector molecules are then provided that will attract two open-ended tubes and bond with the exposed bonding sites, thus providing a linked CNT structure. This process can be used to create ropelike CNT structures. Such ropelike CNT structures tend to tangle, so, here too, the limited ability to orient the CNT structures is a significant impediment to application development.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

[0007] The invention may be best understood by referring to the following description and accompanying drawings that are used to illustrate embodiments of the invention. In the drawings:

[0008] Figure 1 illustrates a process for producing 3D nanotube structures in accordance with one embodiment of the invention;

[0009] Figures 2A - 2D illustrate the layers of a cone-shaped connector molecule that can be used to connect CNTs to form a 3D nanotube structure in accordance with one embodiment of the invention;

[0010] Figures 3A and 3B illustrate respective views of a  $C_{19}S_6H_{24}$  molecule that can be used as a connector molecule to produce 3D nanotube structures in accordance with one embodiment of the invention;

[0011] Figure 4 illustrates the connection of coned-topped nanotube segments to form a 3D nanotube structure in accordance with one embodiment of the invention; and

[0012] Figure 5 illustrates a process for fabricating a microchannel device from a composite polymer incorporating 3D nanotube structures in accordance with one embodiment of the invention.

## **DETAILED DESCRIPTION**

[0013] In the following description, numerous specific details are set forth. However, it is understood that embodiments of the invention may be practiced without these specific details. In other instances, well-known circuits, structures and techniques have not been shown in detail in order not to obscure the understanding of this description.

[0014] Reference throughout the specification to “one embodiment” or “an embodiment” means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” in various places throughout the specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

[0015] Moreover, inventive aspects lie in less than all features of a single disclosed embodiment. Thus, the claims following the Detailed Description are hereby expressly incorporated into this Detailed Description, with each claim standing on its own as a separate embodiment of this invention.

[0016] In accordance with one embodiment of the invention, a connector molecule is provided that bonds with nanotubes to form a three-dimensional (3D) nanotube structure.

[0017] Figure 1 illustrates a process for producing 3D nanotube structures in accordance with one embodiment of the invention. Process 100, shown in Figure 1, begins at operation 105 in which nanotube dimensions (e.g., diameter and length) are determined. The nanotube dimensions may be determined based upon a specific

application, commercially available nanotubes, or other considerations, including those discussed below.

[0018] At operation 110, a desired number of nanotubes are opened to produce open-ended nanotube segments (segments). Opening the nanotubes may be accomplished through an acid washing process (e.g., exposure to nitric acid), as known in the art.

[0019] At operation 115, a connector molecule is determined, such that the shape of the connector molecules allows for the formation of a 3D nanotube structure. For one embodiment, the connector molecules used have one dimension corresponding to the diameter of the nanotubes and another dimension tapered to a significantly smaller size. Therefore, it may be practical to select the nanotube diameter based upon the dimensions of the desired, or available, connector molecules, or vice versa.

[0020] At operation 120, a corresponding number of connector molecules are brought in to contact with the segments. The segments will bond with the connector molecules to form 3D nanotube structures.

[0021] At operation 125, any misbonded segments are filtered. That is, the bonding process may not be completely optimal, resulting in segments and/or connector molecules not bonding, or bonding in an undesired manner.

#### **CONNECTOR MOLECULE**

[0022] For one embodiment, the connector molecule is a cone-shaped molecule, chemically and geometrically matched to a particular nanotube. For example, for one embodiment, the connector molecule for a CNT is cone-shaped, with a ring of carbon atoms forming the base of the cone. The diameter of the base of the cone is matched to the diameter of the CNT. For one embodiment, the point of the cone is a single molecule,

which is capable of bonding to the single molecule points of other cone-shape connector capped nanotube segments.

**[0023]** Figures 2A - 2D illustrate the layers of a cone-shaped connector molecule,  $C_{19}S_6H_{24}$ , that can be used to connect CNTs to form a 3D nanotube structure in accordance with one embodiment of the invention.

**[0024]** Figure 2A illustrates the base, or first layer, of the cone-shaped connector molecule. As shown in Figure 2, the connector molecule has a base ring of sulfur atoms 203, each of which is bonded to two of the carbon atoms 201 that form the edge of CNT segment 202. The base ring of sulfur atoms 203 is matched to the diameter of the nanotube edge 202. In the case illustrated in Figure 2A, the CNT segment has twelve carbon atoms resulting in a CNT diameter of approximately 1.4 nm diameter. Each of the sulfur atoms 203 is double bonded to one of the carbon atoms 204. Each of the carbon atoms 204 is also bonded to one hydrogen atom 205, and also has one remaining bonding pair.

**[0025]** Figure 2B illustrates the second layer of the cone-shaped connector molecule. Each of the second layer carbon atoms 206 is bonded to a first layer carbon atom 204 and two second layer hydrogen atoms 207. Each of the second layer carbon atoms 206 is also bonded to one of three third layer carbon atoms 208. The third layer carbon atoms 208 are below the second layer carbon atoms 206 and form an inverted tetrahedral structure.

**[0026]** Figure 2C illustrates the third layer of the cone-shaped connector molecule. The third layer has three carbon atoms 208 and three hydrogen atoms (not shown). Each carbon atom 208 is bonded to two second layer carbon atoms, as discussed above in reference to Figure 2B, and also to a one hydrogen atom. This leaves one bonding pair

per carbon atom free (tetrahedral, inverted). This free bond from each of the three third layer carbon atoms is joined to a single carbon atom (fourth layer, discussed below).

**[0027]** Figure 2D illustrates the fourth layer of the cone-shaped connector molecule. A single carbon atom 209 is bound to three third layer carbon atoms (not shown) and to a  $C_3H_3$  group 210. The final (point) carbon atom 211 may be bound to any other group or cone-capped nanotube segment to produce a 3D nanotube structure. Since the point carbon atom 211 has only two of its eight valence electrons engaged in the bonding to  $C_3H_3$  group 210, it can accommodate a bonding with the point carbon atoms from three other cone-shaped connector molecules.

**[0028]** Figures 3A and 3B illustrate respective views of a  $C_{19}S_6H_{24}$  molecule that can be used as a connector molecule to produce 3D nanotube structures in accordance with one embodiment of the invention. Figure 3A shows the side view of cone-shaped connector molecule 301. Figure 3B shows the top view of cone-shaped connector molecule 301.

**[0029]** Figure 4 illustrates the connection of coned-topped nanotube segments to form a 3D nanotube structure in accordance with one embodiment of the invention. 3D nanotube structure 400, shown in Figure 4, includes four nanotube segments 405a - 405d. The end of each nanotube segment has been cut and a cone-shaped connector molecule has been attached to each end as described above. For one embodiment, as shown in Figure 4, the connector molecules 406, which need not be cone-shaped, are shaped to provide enough physical space for the connection of multiple nanotube segments 405a - 405d. Additionally, the connector molecules 406 are chemically constituted to provide bonding sites to connect multiple connector molecules.



[0030] For one embodiment, the cone-shaped connector molecule has a base equal to the diameter of the nanotube and tapers to a single molecule point, which can be connected to the points of other cone-shaped connector molecules. For one embodiment, the dimensions of the connector molecule are based, not only upon the diameter of the nanotubes, but on the length of the nanotubes as well.

[0031] When the 3D nanotube structure has reached a desired size, the connection process can be halted, by providing an atom or molecule to cap the open ends of remaining nanotube segments. That is, for example, an atom without sufficient additional bonding sites to promote continued connections is used to cap the open ends of the remaining nanotube segments.

#### **EXEMPLARY APPLICATIONS**

[0032] The 3D nanotube structure, in accordance with various embodiments, has many applications. For one embodiment, the 3D nanotube structures may be incorporated into a base material (e.g., a polymer or ceramic) to provide a material with improved thermal conductivity. That is, because thermally conductive materials are more efficient if heat is conducted in all directions (as opposed to along a path), the 3D nanotube structure, when incorporated into a material, in accordance with various embodiments of the invention, provide greatly improved thermal conductivity. Additionally, the thermal conductivity of a polymer can be adjusted by the addition of more or less 3D nanotube structures, in accordance with one embodiment of the invention.

## Microchannel

**[0033]** A microchannel cold plate (microchannel) is a heat dissipation device used to cool integrated circuits (ICs). Microchannel devices have a series of very small channels through which a fluid (coolant) is flowed to dissipate heat. The fluid channels are typically 50 - 60 microns in diameter. Currently, the microchannel devices are made by chemically etching silicon to form the fluid channels, or alternatively, by laser drilling, or acid-etching copper. Such processes are relatively costly, often employ harsh chemicals, and provide limited flexibility in fluid channel design. Moreover, a thermal interface material (TIM) must be used to bond the microchannel to the IC package.

**[0034]** In accordance with one embodiment of the invention, a thermally conductive polymer incorporating 3D nanotube structures is used to form a microchannel. The microchannel device can be formed by molding, casting, or extruding the polymer and the fluid channels can be formed by a wet etch process. For one embodiment, the microchannel device is cast directly on the IC package, thus eliminating the need for the TIM at that interface.

**[0035]** Use of a polymer incorporating 3D nanotube structures to form a microchannel also allows the thermal conductivity to be adjusted by varying the volume percentage of 3D nanotube structures in the polymer matrix.

**[0036]** Figure 5 illustrates a process for fabricating a microchannel device from a composite polymer incorporating 3D nanotube structures in accordance with one embodiment of the invention. Process 500, shown in Figure 5, begins at operation 505 in which a number of slabs of a composite polymer/3D nanotube structure material are formed. The slabs can be of varying thickness.

[0037] At operation 510, a series of wires are placed between stacked slabs. The wires, which will form the fluid channels of the microchannel device, can be of varying diameter and may be patterned as desired.

[0038] At operation 515, the stack of slabs, with the wires positioned between each slab, are bonded such that the wires are embedded in a continuous slab that forms the microchannel device. In one embodiment, the stack of slabs may be chemically bonded.

[0039] At operation 520, the wires are heated and removed from the continuous slab. For one embodiment, a voltage is applied and an electrical current passed through the wires to locally soften or melt the polymer so that the wires can be removed. In an alternative embodiment, the polymer may be heated to conform to the wires or to allow removal of the wires.

[0040] The removal of the wires leaves fluid channels that may be any desired shape or size without extensive processing or retooling. This allows for a great deal of flexibility in designing the microchannel device. With such flexibility, and the ability to adjust the thermal conductivity of the composite material, the microchannel can be designed to closely match the heat signature of a given IC device.

#### Cold Plate and Heat Exchanger

[0041] Cold plates also are liquid cooled heat dissipation devices for ICs, but with much larger channels than a microchannel device. In a typical configuration, an IC device chip package is thermally coupled to an integrated heat spreader (IHS) using a TIM. The cold plate is on top of the (IHS) with another layer of TIM between them. A coolant (e.g., water or water/propylene glycol mixture) is pumped into the cold plate. Heat is transferred from the chip package through the IHS to the coolant of the cold plate.

The coolant is pumped out of the cold plate to a liquid/air heat exchanger where it is dissipated.

[0042] Typically, cold plates are made of copper or aluminum and are machined or stamped. To achieve desired heat removal, several thin fins are bundled closely together. The desired fin proximity may make machining difficult, or preclude it entirely. In the latter case, the fins are typically attached to a separate base plate. Where the fins are brazed, there is additional thermal resistance.

[0043] In accordance with one embodiment of the invention, a cold plate and heat exchanger are formed from a composite polymer incorporating 3D nanotube structures. For one embodiment, the cold plate may be formed by molding, casting, or extruding the polymer. The heat exchanger, owing to its more complicated form, may be molded or built from smaller pieces of the polymer. Because it may be molded or cast, it is possible to design more intricate cold plates. The coolant tube and the fins can be cast as one piece, thus reducing fabrication costs and complexity. The TIM material can be eliminated because the cold plate can be chemically bonded to the IHS or the silicon directly.

#### Heat Sink and Integrated Heat Spreader

[0044] Heat sinks are larger heat dissipation devices that are typically made of machined metal (e.g., copper). Machining is an expensive process that does not lend itself to intricate design. The IHS is also typically copper and is thermally coupled with the IC device with a TIM (e.g., thermal grease). The TIMs may be poor thermal conductors and be the cause of thermal bottleneck in the overall heat dissipation stack-up.

Also, the IHS typically has a rough surface that makes it difficult to mate with the heat sink surface.

[0045] In accordance with one embodiment of the invention, a heat sink and IHS are formed from a composite polymer incorporating 3D nanotube structures. For one embodiment, either the heat sink, the IHS, or both, may be formed by molding, casting, or extruding the polymer. Heat sinks formed from such a polymer are lighter and can be formed in more intricate shapes. Again, the thermal conductivity can be adjusted by varying the amount of 3D nanotube structures present in the composite polymer, as discussed above, in reference to the microchannel device.

[0046] For one embodiment, a composite polymer IHS can be bonded directly to the IC package or the heat sink, thus eliminating the need for, and the difficulties associated with, the TIM. Also, in accordance with one embodiment, a localized liquid solvent may be used at the interface between the heat sink and the IHS to liquefy the composite polymer. As the solvent evaporates, the composite polymer solidifies in direct contact with the bonding surface allowing the composite polymer to more fully conform to the bonding surface, thus eliminating the need for the TIM.

#### **GENERAL MATTERS**

[0047] Embodiments of the invention provide molecular structures and methods to create 3D nanotube structures. That is, by creating or determining an appropriate connector molecule, nanotubes (e.g., carbon nanotubes) may be connected in 3D shapes that provide desired electrical, thermal, and mechanical properties.

[0048] Embodiments of the invention have been described in which the connector molecule is cone-shaped. For various alternative embodiments, the connector molecule may be some other shape that allows the formation of a 3D nanotube structure.

[0049] Embodiments of the invention have been described in terms of various applications that take advantage of the improved thermal conductivity provided by composite polymers containing a 3D nanotube structure. It is apparent to one skilled in the art that embodiments of the invention have wide-ranging application, beyond composite polymers, that use additional or alternative characteristics of the 3D nanotube structure.

[0050] Embodiments of the invention include various operations. Many of the methods are described in their most basic form, but operations can be added to or deleted from any of the methods without departing from the basic scope of the invention.

[0051] While the invention has been described in terms of several embodiments, those skilled in the art will recognize that the invention is not limited to the embodiments described, but can be practiced with modification and alteration within the spirit and scope of the appended claims. The description is thus to be regarded as illustrative instead of limiting.